

OH RADICAL GENERATION BY ATMOSPHERIC PRESSURE PLASMA AND ITS QUANTITATIVE ANALYSIS BY MONITORING CO OXIDATION

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Introduction

Applications of non-thermal plasma for gaseous pollution control or methanol synthesis have been carried out by several researchers [1,2]. In these plasma chemical reactions, OH radicals play a very important role for their strong oxidation capability. In understanding the mechanism of plasma chemical reactions, the behavior of the OH radical in both formation process and the subsequent chemical reaction process is required to be known. The measurement of OH radicals in discharge plasma, however, is very difficult, especially under the atmospheric condition. There are several methods such as LIF (Laser-induced fluorescence) or OES (Optical emission spectroscopy). These methods require rather complicated measurement system.

In the atmospheric chemistry, the CO oxidation monitoring method has been used to measure OH radicals concentration [3]. In this paper, the application of CO oxidation monitoring method to the OH radicals measurement in a pulsed discharge plasma in argon and H₂O mixture at atmospheric pressure was examined.

When a pulsed discharge plasma is generated in H₂O/Ar, OH radicals are formed by the collisions of electrons or the excited Ar molecules with H₂O. If CO was added to H₂O/Ar, it will be rapidly oxidized by OH radicals as shown in reaction (1). According to this reaction, the concentration of OH radicals can be determined by the amount of produced CO₂.



In order to apply this method in the discharged plasma, it is necessary to consider both the dissociation of CO₂ due to the next pulse discharge and the loss reactions of OH radicals. Under a condition where these influences can be ignored, the concentration of OH radicals can be determined as CO₂ concentration. In this work, gas residence time and initial CO concentration necessary to ignore the dissociation of CO₂ was studied with experiment and calculation. On the basis of this method, the concentration of OH radicals in the H₂O/Ar plasma was measured to study the effect of H₂O content, SIE on the formation of OH radicals.

Experimental

The gas mixture of Ar (99.999%) and CO (99.95%) was adjusted using mass flow controllers (Estec Inc., SEC-410 and DS-3). The H₂O concentration was controlled by evaporating a constant rate of H₂O fed by a microfeeder. The gas temperature was controlled by a convection oven (SIBATA, SPF-600) and a ribbon heater. The gas-residence time was adjusted by changing the flow rate of gas. A square pulse high voltage (peak voltage 15-22kV, frequency 230-240Hz) was used to form non-thermal pulsed discharge plasma.

The reaction products were analyzed by FT-IR (BIO-RAD, FTS-30) and found to be CO and CO₂. A GC-FID (Shimadzu, GC-8A) equipped with a methanizer (GL Sciences, MT-221) was used for quantitative measurement of CO and CO₂. The voltage and current waveform were recorded with a digital oscilloscope (Tektronix, TDS-644A), a voltage divider (Tektronix, P6015) and

a current probe (Tektronix, P6021). The discharge power was calculated with voltage and current waveform.

Results and Discussion

A. Criteria of the method

Dissociation of CO₂ due to discharge. In the case of the pulsed discharge plasma, the dissociation of products is mainly caused when the products are exposed to the plasma. For the purpose of quantitative measurement of OH radicals, unless otherwise noted, experiments were carried out in a single pulse condition, to avoid the dissociation of products. The single pulsed discharge process was realized by adjusting the gas-residence time to the period of the applied voltage. Consequently, there will be no dissociation of CO₂ caused by the next pulse. The time evolution of CO₂ production of the reaction of CO and OH was calculated. **Fig. 1** indicates that 130μs was necessary for the reaction to reach an equilibrium state when the OH concentration was 50ppm and the CO concentration was 1%. Because the FWHM (Full width at half-maximum) of the pulse current was 40ns, the reaction of CO and OH ran at the interval term of two successive pulsed discharges. The oxidation of CO by OH can be considered as a chemical reaction, and it is not affected from discharge in the single pulsed discharge.

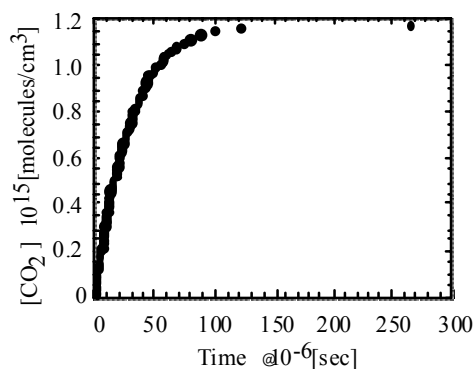


Fig.1 Calculation for the reaction time of CO₂ production.

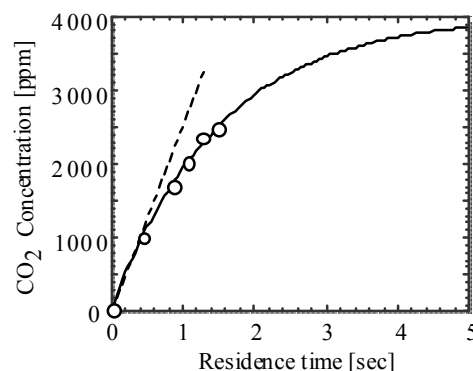
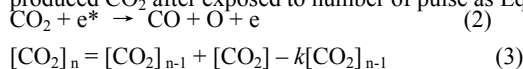


Fig. 2 Influences of the dissociation of CO₂ by discharge. (Discharge power=3.1W, H₂O/CO/Ar=1/1/98)

Under extended gas residence time, however, both processes of CO₂ formation and CO₂ dissociation take place at the same time. In this sense, we should consider these both processes to estimate the produced CO₂ concentration. Assuming that the production of CO₂ per each single pulse is constant and the dissociation of CO₂ is caused by reaction (2), then we can obtain the concentration of produced CO₂ after exposed to number of pulse as Eq. (3).



$$[\text{CO}_2]_n = [\text{CO}_2]_{n-1} + [\text{CO}_2] - k[\text{CO}_2]_{n-1} \quad (3)$$

Where

$[\text{CO}_2]$ = CO_2 production by a single pulse

$[\text{CO}_2]_{n-1}$ = CO_2 production by n-1 times of pulses

k = The rate of the dissociation of CO_2 by a single pulse discharge

Eq. (3) is transformed into Eq. (4).

$$[\text{CO}_2]_n = [\text{CO}_2] \times k^{-1} \times [1 - (1-k)^n] \quad (4)$$

It indicates that $[\text{CO}_2]_n$ increases with the number of pulse (the residence time) nonlinearly. Fig.2 shows the experimental results of the gas residence time up to 1.6sec. CO_2 production, $[\text{CO}_2]_n$, tends to increase linearly with the residence time up to 0.5sec, and then begin to saturate. The appearance of the linear increasing of CO_2 indicates that, the influence of the dissociation of CO_2 caused by succeeding discharges can be ignored when the residence time smaller than 0.5sec in this experimental condition.

The influences of loss reactions of OH radicals. Differing from the chemistry of atmospheric space, concentration of OH radical in the discharge plasma is very high. In the conditions where the concentration of OH radical is high, the loss-reaction mainly due to recombination may take place. Reactions (5)-(10) are regarded main reactions in the discharge space where H_2O exists. Reactions (5)-(8) are the loss-reactions of OH radicals. These reactions compete with the reaction (1), and affect the CO oxidation by OH radicals. OH radicals branching depends on the rate constants and initial concentrations of CO and OH. The variation of CO_2 production with the variation of the CO initial concentration was measured by the experiment. Calculation was also made using a simulation software (IBM, CKS version 1.0).

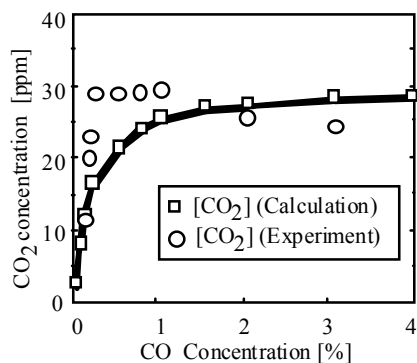


Fig.3 The influence of OH loss reactions. (Calculation condition: reaction (1), (5) -(10) were used. $[\text{OH}]_0 = [\text{H}]_0 = 8.1 \times 10^{14}$ molecules/cm³, $[\text{CO}]_0 = 2.7 \times 10^{14}$ molecules/cm³, $[\text{H}_2\text{O}]_0 = 2.7 \times 10^{14}$ molecules/cm³, Experimental condition: Content of H_2O = 1%, Residence time = 4.2ms, Discharge power = 1.8W, T = 50 degree)

Fig.3 shows the results of the experiment and the simulation. In the experiment, the CO_2 production was observed while the initial concentration of CO was varied from 800ppm to 4%. When $[\text{CO}]_0 < 2000\text{ppm}$, the CO_2 production was increased with increasing $[\text{CO}]_0$. When $[\text{CO}]_0 \geq 2000\text{ppm}$, the CO_2 concentration became constant. This result indicated that the influence of the loss-reactions of OH radicals could be ignored when initial CO concentration is higher than 2000ppm. However, when CO concentration exceeded 1%, the CO_2 concentration

began to decrease because the peak discharge current decreased.

The result shows the similar tendency in the variation of the CO_2 formation. It indicates that the influence of loss reactions much depends on the initial concentration of CO.

B. Influences of H_2O content and discharge power on OH formation

Fig.4 shows the relation between the H_2O content and the OH formation. It shows that production of OH radicals increased when the H_2O content increased under the same SIE (Specific Input Energy: energy to unit volume of gas, kJ/m³). The production of OH radical increased with the SIE value when the H_2O content was kept constant. These results agree with other measurements on spectroscopic analysis of OH formation in DBD (dielectric barrier discharges) of Ar/ O_2 / H_2O [4].

In our experiment, under the conditions with the SIE value of 9 kJ/m³ and H_2O content of 1.5%, the maximum OH production 30ppm (9.4×10^{14} cm⁻³) was obtained. The value is about the same as that observed in DBD [5]. In our experiment, the G value, which is defined as the number of OH produced per 100 eV, is 1.9. Penetrante calculated the G value for OH generation using DEGARD in the case of pure H_2O , and obtained 1.42[1]. It should be noted that a comparable OH yield-value has been obtained in our experiment using the simple equipment.

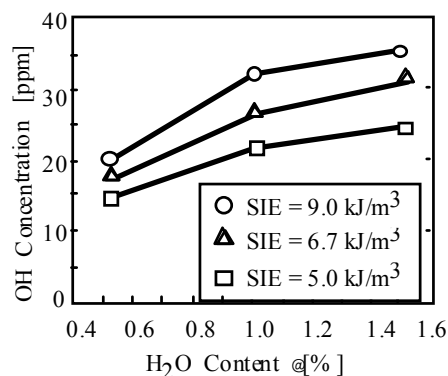


Fig.4 Influences of OH formation according to the variation of content of H_2O and discharge power. ($\text{CO}/\text{Ar} = 1\%$, T = 50 degree)

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